Supporting Information

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I. General Information

a). Materials

All the reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity \geq 99.999%). The following chemicals were purchased and used as received: NiBr₂·diglyme (Aldrich), 4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine (Aldrich), Anhydrous N,N-Dimethylacetamide (99.8%, HY Scientific), Anhydrous DMF (Aldrich), Triethoxysilane (95%, TCI), Diethoxymethylsilane (97%, adamas-beta), 1-Phenyl-1-propyne (95%, TCI), 4-Octyne (99%, TCI), oct-1-yne (95%, TCI).

b). Analytical Methods

¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl₃ unless otherwise noted; Data for ¹H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

II. Preparation of Substrates

N-(2-iodopropyl)-N-methylaniline CAS: 1604039-11-3

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.19 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 2H), 4.44 – 4.26 (m, 1H), 3.93 – 3.77 (m, 1H), 3.56 – 3.42 (m, 1H), 2.99 (s, 3H), 1.87 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 129.3, 116.9, 111.8, 63.1, 39.8, 25.9, 25.9.



1-(3-iodobutyl)-4-methoxybenzene CAS: 1383841-50-6

¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 4.08 – 3.97 (m, 1H), 3.72 (s, 3H), 2.75 – 2.67 (m, 1H), 2.62 – 2.51 (m, 1H), 2.18 – 2.00 (m, 1H), 1.87 (d, J = 6.8 Hz, 3H), 1.80 – 1.70 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 158.0, 132.8, 129.5, 114.0, 55.3, 44.7, 35.0, 29.9, 29.1



3-iodo-1-tosylpyrrolidine CAS: 919284-59-6

¹H NMR (400 MHz, CDCl3): δ7.74 (d, J = 8.19 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.15 – 4.14 (m, 1H), 3.90 (dd, J = 11.7, 5.9 Hz, 1H), 3.55 (dd, J = 11.7, 4.8 Hz, 1H), 3.43 (dd, J = 7.4, 6.1 Hz, 2H), 2.43 (s, 3H), 2.31-2.20 (m, 1H), 2.17-2.07 (m, 1H).

¹³C NMR (101 MHz, CDCl3): δ 143.77, 133.91, 129.81, 127.58, 58.63, 46.97, 38.12, 21.55, 17.26.



(4-iodopiperidin-1-yl)(phenyl)methanone CAS: 244240-61-7

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.34 (m, 5H), 4.58 – 4.46 (m, 1H), 4.02 – 3.85 (m, 1H), 3.69 – 3.46 (m, 2H), 3.38 – 3.25 (m, 1H), 2.30 – 1.88 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 170.56, 135.71, 129.83, 128.61, 126.91, 47.71, 42.20, 37.94, 37.16, 26.78.

Ts

4-iodo-1-tosylpiperidine CAS: 289890-80-8

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.33 – 4.22 (m, 1H), 3.20 – 3.12 (m, 2H), 3.05 – 2.88 (m, 2H), 2.44 (s, 3H), 2.17 – 2.06 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 143.9, 133.5, 129.9, 127.8, 45.8, 36.6, 25.7, 21.7.



benzyl 3-iodoazetidine-1-carboxylate CAS: 939759-26-9

¹H NMR (400 MHz, CDCl3): δ 7.39 – 7.30 (m, 5H), 5.11 (s, 2H), 4.75 – 4.71 (m, 2H), 4.54 – 4.47 (m, 1H), 4.38 – 4.35 (m, 2H).

¹³C NMR (101 MHz, CDCl3): δ 155.81, 136.30, 128.55, 128.20, 128.07, 67.01, 61.75, 2.25.

(3aR,5aR,8aR,8bS)-3a-(iodomethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran CAS: 940006-45-1

¹H NMR (400 MHz, CDCl₃) δ 4.59 (dd, J = 7.9, 2.7 Hz, 1H), 4.31 (d, J = 2.7 Hz, 1H), 4.23 (dd, J = 7.9, 1.2 Hz, 1H), 3.91 (dd, J = 13.0, 1.9 Hz, 1H), 3.79 (dd, J = 13.0, 0.6 Hz, 1H), 3.54 (d, J = 10.7 Hz, 1H), 3.34 (d, J = 10.7 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H).

¹³C NMR (101 MHz, CDCl3): δ 109.39, 108.59, 100.43, 72.01, 70.84, 70.74, 62.13, 26.69, 26.15, 25.41, 24.36, 10.85.

4-iodoheptane

¹H NMR (400 MHz, CDCl₃) δ 4.27 – 4.01 (m, 1H), 1.93 – 1.77 (m, 2H), 1.70 – 1.61 (m, 2H), 1.59 – 1.51 (m, 2H), 1.47 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 42.88, 40.18, 22.92, 13.41.



1-(3-iodopropoxy)-4-methoxybenzene

¹H NMR (400 MHz, CDCl₃) δ 6.99 – 6.65 (m, 4H), 4.07 – 3.88 (m, 2H), 3.77 (s, 3H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.25 (dq, *J* = 12.5, 6.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.11, 152.93, 115.69, 114.79, 68.10, 55.87, 33.21, 2.86.

Bn_N Ph Br

N-benzyl-2-bromo-N-phenylbutanamide CAS: 851073-30-8

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 6.92 (m, 10H), 4.90 (q, J = 14.2 Hz, 2H), 4.07 – 3.84 (m, 1H), 2.26 – 2.09 (m, 1H), 2.05 – 1.78 (m, 1H), 0.89 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.03, 141.11, 136.91, 129.74, 128.88, 128.63, 128.49, 128.38, 127.60, 53.57, 46.04, 28.69, 12.17.



1-((3R,88,98,10R,138,148,178)-3-iodo-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetr adecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one

¹H NMR (400 MHz, CDCl₃) δ 5.40 – 5.27 (m, 1H), 4.12 – 3.94 (m, 1H), 2.92 (ddd, J = 16.0, 5.2, 2.6

Hz, 1H), 2.73 – 2.63 (m, 1H), 2.59 – 2.46 (m, 1H), 2.38 – 2.11 (m, 5H), 2.08 – 1.92 (m, 2H), 1.80 – 1.37 (m, 9H), 1.31 – 1.11 (m, 3H), 1.07 – 0.94 (m, 4H), 0.63 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 209.51, 142.81, 121.46, 63.72, 56.90, 50.28, 46.40, 44.03, 41.97, 38.80, 36.59, 36.56, 31.67, 31.65, 30.21, 24.54, 22.89, 20.87, 19.33, 13.31.



4-(oct-1-yn-1-yl)benzonitrile CAS: 312708-98-8

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.42 – 7.36 (m, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.53 (dd, *J* = 14.5, 7.1 Hz, 2H), 1.37 (ddd, *J* = 13.4, 9.3, 7.1 Hz, 2H), 1.25 (dt, *J* = 7.5, 3.6 Hz, 4H), 0.87 – 0.81 (m, 3H).

(Reference: J. Org. Chem. 2008, 73, 9061-9064)



ethyl 3-(oct-1-yn-1-yl)benzoate CAS: 1648789-05-2

¹H NMR (400 MHz, CDCl₃) δ 8.06 (t, J = 1.6 Hz, 1H), 7.99 – 7.89 (m, 1H), 7.58 – 7.50 (m, 1H), 7.36 (dd, J = 9.8, 5.7 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 1.66 – 1.54 (m, 2H), 1.50 – 1.43 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.35 – 1.30 (m, 4H), 0.96 – 0.86 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.25, 135.78, 132.77, 130.73, 128.61, 128.40, 124.61, 91.69, 79.84, 61.25, 31.51, 28.77, 22.71, 19.54, 14.46, 14.22, 0.14.



1-(3-(oct-1-yn-1-yl)phenyl)ethan-1-one CAS: 911056-45-6

¹H NMR (400 MHz, CDCl₃) δ 7.97 (t, J = 1.6 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.61 – 7.52 (m, 1H), 7.42 – 7.35 (m, 1H), 2.60 (s, 3H), 2.42 (t, J = 7.1 Hz, 2H), 1.67 – 1.58 (m, 2H), 1.46 (ddd, J = 13.4, 9.4, 7.1 Hz, 2H), 1.33 (dt, J = 7.4, 3.6 Hz, 4H), 0.95 – 0.87 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 197.61, 137.07, 135.89, 131.56, 128.53, 127.09, 124.72, 91.78, 79.65, 31.36, 28.63, 28.62, 26.66, 22.57, 19.40, 14.08.



1-(hex-1-yn-1-yl)-4-(trifluoromethyl)benzene

¹H NMR (400 MHz, CDCl₃) δ 7.54-7.45 (m, 4H), 2.43 (t, J = 7.0 Hz, 2H), 1.62 -1.55(m, 2H), 1.52-1.44 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). (Reference: *Org. Let.* **2014**,*16*, 3776-3779)

2-(oct-1-yn-1-yl)naphthalene

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.78 (ddd, *J* = 13.1, 9.5, 6.5 Hz, 3H), 7.51 – 7.38 (m, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.65 (dt, *J* = 14.8, 7.1 Hz, 2H), 1.49 (dq, *J* = 10.0, 7.1 Hz, 2H), 1.40 – 1.28 (m, 3H), 1.40 – 1.28 (m, 3H), 3.40 – 3.40 (m, 3H), 3.40 (m, 3H), 3.40 – 3.40 (m, 3H), 3.40 (m, 3H),

4H), 0.93 (dd, *J* = 9.4, 4.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 133.04, 132.42, 130.98, 128.74, 127.77, 127.68, 127.56, 126.33, 126.20, 121.41, 90.92, 80.87, 31.40, 28.77, 28.66, 22.59, 19.53, 14.10.



3-(hept-1-yn-1-yl)pyridine

¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 8.48 (d, J = 4.9 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.16 (dd, J = 7.8, 4.8 Hz, 1H), 2.42 (t, J = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H).

(Reference: Org. Let. 2004, 6, 3481-3484)



1-chloro-4-(hept-1-yn-1-yl)benzene

¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 2.38 (t, J = 6.8 Hz, 2H), 1.57-1.64 (m, 2H), 1.31-1.44 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H), (Reference: *Angew. Chem. Int. Ed.* **2010**, *49*, *1278-1281*)

III. General Experimental Procedures, Spectral Data and HPLC

Date and X-Ray Structure

a) Experimental Procedures

Experimental Procedures for Examples Described in Table 1.

In air, catalyst (10 mol%), base (2.5 equiv.), ligand (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol iodocyclohexane and 1-Phenyl-1-propyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc. Benzophenone was added as an internal standard. The yield was determined by GC.

Experimental Procedures for Examples Described in Table 2.

In air, NiBr₂·diglyme (10 mol%), K₂CO₃ (2.5 equiv.), dtbbpy (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.7 ml DMAc was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol alkyl halide and alkyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Scheme 2.

(1) In air, NiBr₂ diglyme (10 mol%), K₂CO₃ (2.5 equiv.), dtbbpy (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.7 ml DMAc was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol fructose derivative and 1-Phenyl-1-propyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

(2) In air, NiBr₂ diglyme (10 mol%), K_2CO_3 (2.5 equiv.), dtbbpy (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.7 ml DMAc was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol pregnenolone derivative and 1,2-diphenylethyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Eq. 1.

In air, NiBr₂ diglyme (10 mol%), K₂CO₃ (2.5 equiv.), dtbbpy (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.7 ml DMAc was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol 4-iodo-1-tosylpiperidine and 1-Phenyl-1-propyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Eq. 2.

In air, NiBr₂·diglyme (10 mol%), K₂CO₃ (2.5 equiv.), dtbbpy (12 mol%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.7 ml DMAc was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2 mmol **2da** and 1-Phenyl-1-propyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 3.0 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

b) Spectral data and HPLC date



(E)-N-(2,3-dimethyl-4-phenylbut-3-en-1-yl)-N-methylaniline

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.05 (m, 7H), 6.83 – 6.59 (m, 3H), 6.27 (br, 1H), 3.45 – 3.27 (m, 2H), 2.94 (s, 3H), 2.78 (dd, *J* = 14.1, 7.0 Hz, 1H), 1.84 (s, 3H), 1.11 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.26, 140.95, 138.45, 129.26, 128.98, 128.13, 126.09, 125.96, 115.82, 111.98, 57.85, 41.96, 39.50, 17.17, 14.92.

HRMS (APCI) calcd for C19H24N (M+H⁺): 266.1903; found: 266.1904.



(E)-1-(3,4-dimethyl-5-phenylpent-4-en-1-yl)-4-methoxybenzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 7.1 Hz, 2H), 7.11 (dd, J = 14.4, 7.2 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 6.22 (br, 1H), 3.70 (s, 3H), 2.50 – 2.39 (m, 2H), 2.23 (dd, J = 14.7, 6.7 Hz, 1H), 1.72 (d, J = 1.1 Hz, 3H), 1.69 – 1.52 (m, 2H), 1.03 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.75, 142.81, 138.72, 134.93, 129.40, 129.07, 128.14, 125.96, 125.03, 113.82, 55.37, 43.31, 37.15, 33.18, 19.92, 14.06.

HRMS (APCI) calcd for C20H25O (M+H⁺): 281.1900; found: 281.1902.



(E)-(2,3-dimethylpent-1-en-1-yl)benzene

Following general procedure, as a pale-yellow liquid. product ratio >35:1. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, J = 7.5 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 6.27 (br, 1H), 2.17 (dd, J = 14.2, 7.0 Hz, 1H), 1.76 (d, J = 1.2 Hz, 2H), 1.52 – 1.34 (m, 3H), 1.08 (d, J = 6.9 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.21, 138.91, 129.08, 128.10, 125.85, 124.56, 45.52, 27.98, 19.53, 14.19, 12.32.

HRMS (APCI) calcd for C13H19 (M+H⁺): 175.1481; found: 175.1480.

(E)-(2-cyclohexylprop-1-en-1-yl)benzene

Following general procedure, as a pale-yellow liquid. product ratio >30:1. ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 6.26 (br, 1H), 2.05 – 1.94 (m, 1H), 1.87 – 1.75 (m, 7H), 1.74 – 1.67 (m, 1H), 1.37 – 1.11 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 144.43, 139.04, 129.07, 128.07, 125.79, 123.13, 48.39, 32.04, 26.89, 26.52, 16.29.

HRMS (APCI) calcd for C15H21 (M+H⁺): 201.1638; found: 201.1645.

(E)- (2-cyclohexylbut-1-en-1-yl) benzene

Following general procedure, as a pale-yellow liquid. product ratio >30:1. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 7.6 Hz, 2H), 7.24 – 7.12 (m, 3H), 6.22 (s, 1H), 2.25 (q, J = 7.5 Hz, 2H), 1.99 (dd, J = 15.4, 6.7 Hz, 1H), 1.82 (dd, J = 9.8, 2.5 Hz, 4H), 1.71 (d, J = 11.5 Hz, 1H), 1.35 – 1.10 (m, 5H), 1.06 (t, J = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.64, 139.10, 128.71, 128.17, 125.84, 122.75, 44.83, 33.14, 27.18, 26.60, 23.75, 13.86.

HRMS (APCI) calcd for C16H22Na (M+Na⁺): 237.1614; found: 237.1615.



(E)-1-(((3,4-dimethyl-5-phenylpent-4-en-1-yl)oxy)methyl)-3-fluorobenzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (dt, J = 9.5, 4.8 Hz, 3H), 7.25 – 7.15 (m, 3H), 7.09 (dd, J = 11.7, 9.0 Hz, 2H), 6.96 (td, J = 8.4, 2.3 Hz, 1H), 6.31 (s, 1H), 4.49 (s, 2H), 3.49 (t, J = 6.7 Hz, 2H), 2.51 (dd, J = 15.1, 6.7 Hz, 1H), 1.84 – 1.65 (m, 5H), 1.12 (d, J = 6.9 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -113.40.

¹³C NMR (101 MHz, CDCl₃) δ 163.08 (d, J = 245.7 Hz), 142.41, 141.47 (d, J = 7.0 Hz), 138.58, 129.97 (d, J = 8.2 Hz), 129.04, 128.14, 126.02, 124.97, 123.05 (d, J = 2.8 Hz), 114.44 (d, J = 21.3 Hz), 72.41, 69.16, 40.52, 34.89, 19.86, 14.05.

HRMS (APCI) calcd for C20H23FNaO (M+Na⁺): 321.1625; found: 321.1622.



(Z)-N-methyl-N-(2-methyl-3,4-diphenylbut-3-en-1-yl)aniline

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.24 (m, 3H), 7.23 – 7.10 (m, 4H), 7.09 – 7.01 (m, 3H), 6.88 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.47 (br, 1H), 3.57 (dd, *J* = 14.2, 4.7 Hz, 1H), 3.09 (ddd, *J* = 13.0, 10.3, 5.3 Hz, 2H), 2.95 (s, 3H), 1.19 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.26, 146.09, 140.87, 137.33, 129.22, 129.18, 129.13, 128.69, 127.97, 127.16, 126.66, 126.41, 115.94, 112.06, 58.53, 41.73, 39.84, 18.05.

HRMS (APCI) calcd for C24H26N (M+H⁺): 328.2060; found: 328.2063.

(E)-3-(1-phenylprop-1-en-2-yl)-1-tosylpyrrolidine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.2 Hz, 2H), 7.31 (dd, J = 17.2, 7.9 Hz, 4H), 7.22 – 7.12 (m, 3H), 6.19 (br, 1H), 3.54 (dd, J = 9.8, 7.8 Hz, 1H), 3.47 (ddd, J = 9.8, 8.4, 3.0 Hz, 1H), 3.27 (td, J = 9.5, 6.8 Hz, 1H), 3.13 (t, J = 9.4 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.42 (s, 3H), 2.04 – 1.96 (m, 1H), 1.82 – 1.70 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 143.54, 137.60, 136.60, 133.94, 129.79, 128.92, 128.15, 127.61, 126.45, 125.78, 51.51, 47.85, 47.46, 30.03, 21.61, 16.06.

HRMS (APCI) calcd for C20H24O2NS (M+H⁺):342.1522; found: 342.1522.



(E)-4-(2-(1-(methyl(phenyl)amino)propan-2-yl)oct-1-en-1-yl)benzonitrile

Following general procedure, as a pale-yellow liquid. product ratio >30:1. ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.49 (m, 2H), 7.34 – 7.13 (m, 4H), 6.69 (dd, J = 7.6, 4.6 Hz, 3H), 6.29 (br, 1H), 3.49 (dd, J = 14.6, 6.5 Hz, 1H), 3.30 (dd, J = 14.6, 7.8 Hz, 1H), 2.97 (s, 3H), 2.81 – 2.70 (m, 1H), 2.28 – 2.12 (m, 2H), 1.44 – 1.39 (m, 2H), 1.29 – 1.20 (m, 6H), 1.17 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 6.9 Hz,

3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.65, 149.18, 143.42, 132.09, 129.31, 129.24, 123.75, 119.30, 116.08, 111.98, 109.57, 59.29, 39.81, 39.14, 31.59, 31.52, 29.62, 28.91, 22.67, 18.51, 14.18. HRMS (APCI) calcd for C25H33N2 (M+H⁺): 361.2638; found: 361.2636.

(E)-1-tosyl-4-(1-(4-(trifluoromethyl)phenyl)hex-1-en-2-yl)piperidine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 6.9 Hz, 2H), 6.23 (s, 1H), 3.92 (d, J = 11.5 Hz, 2H), 2.44 (s, 3H), 2.33 – 2.22 (m, 2H), 2.21 – 2.11 (m, 2H), 1.97 – 1.87 (m, 1H), 1.84 (d, J = 12.9 Hz, 2H), 1.70 (td, J = 12.5, 3.7 Hz, 2H), 1.40 – 1.29 (m, 2H), 1.28 – 1.18 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.11.

¹³C NMR (101 MHz, CDCl₃) δ 148.52, 143.63, 142.01, 133.24, 129.76, 128.92, 128.27 (q, *J* = 32.4 Hz), 127.91, 125.15 (q, *J* = 3.8 Hz), 124.42 (q, *J* = 271.7 Hz), 123.34, 47.02, 42.23, 31.24, 31.11, 30.50, 23.00, 21.68, 13.97.

HRMS (APCI) calcd for C25H30F3NNaO2S (M+Na⁺): 488.1842; found: 488.1840.



Ethyl (E)-3-(2-(1-(methyl(phenyl)amino)propan-2-yl)oct-1-en-1-yl)benzoate

Following general procedure, as a pale-yellow liquid. product ratio >35:1. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, *J* = 6.0, 4.0 Hz, 2H), 7.53 – 7.33 (m, 2H), 7.24 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.74 – 6.64 (m, 3H), 6.33 (br, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.50 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.30 (dd, *J* = 14.6, 8.1 Hz, 1H), 2.98 (s, 3H), 2.78 – 2.69 (m, 1H), 2.34 – 2.12 (m, 2H), 1.48 – 1.35 (m, 5H), 1.33 – 1.13 (m, 6H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.83, 149.22, 148.28, 138.72, 133.02, 130.47, 129.66, 129.26, 128.25, 127.30, 124.09, 115.89, 111.91, 61.05, 59.41, 39.84, 38.86, 31.66, 31.44, 29.63, 29.03, 22.69, 18.62, 14.46, 14.19.

HRMS (APCI) calcd for C27H38O2N (M+H⁺): 408.2897; found: 408.2892.



(E)-1-(3-(2-(1-(methyl(phenyl)amino)propan-2-yl)oct-1-en-1-yl)phenyl)ethan-1-one

Following general procedure, as a pale-yellow liquid. product ratio >30:1. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.69 (m, 2H), 7.40 (dd, J = 13.2, 6.1 Hz, 2H), 7.33 – 7.13 (m, 2H), 6.73 – 6.65 (m, 3H), 6.34 (br, 1H), 3.51 (dd, J = 14.6, 6.3 Hz, 1H), 3.30 (dd, J = 14.6, 8.1 Hz, 1H), 2.99 (s, 3H), 2.75 (dd, J = 14.2, 7.3 Hz, 1H), 2.60 (s, 3H), 2.37 – 2.07 (m, 2H), 1.52 – 1.37 (m, 2H), 1.37 – 1.20 (m, 6H), 1.17 (d, J = 6.9 Hz, 3H), 0.85 (t, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 198.37, 149.25, 148.43, 139.01, 137.16, 133.28, 129.28, 128.58, 128.50,

126.11, 124.11, 115.93, 111.94, 59.37, 39.81, 38.85, 31.68, 31.45, 29.67, 29.07, 26.80, 22.68, 18.62, 14.19.

HRMS (APCI) calcd for C26H36ON (M+H⁺): 378.2791; found: 378.2785.

(E) - phenyl (4-(1-phenyl prop-1-en-2-yl) piperidin-1-yl) methan one

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.17 (m, 3H), 6.31 (br, 1H), 4.95 – 4.67 (m, 1H), 3.95 – 3.76 (m, 1H), 3.19 – 2.95 (m, 1H), 2.89 – 2.60 (m, 1H), 2.40 – 2.20 (m, 1H), 1.96 – 1.41 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 170.42, 141.42, 138.24, 136.38, 129.59, 128.99, 128.53, 128.13, 126.96, 126.19, 124.44, 48.35, 46.31, 42.80, 31.44, 30.70, 16.18.

HRMS (APCI) calcd for C21H24ON (M+H⁺):306.1852; found: 306.1849.



benzyl (E)-3-(1-phenylprop-1-en-2-yl)azetidine-1-carboxylate

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 7H), 7.28 – 7.16 (m, 3H), 6.33 (br, 1H), 5.12 (s, 2H), 4.19 (t, *J* = 8.7 Hz, 2H), 4.02 (dd, *J* = 8.8, 6.4 Hz, 2H), 3.42 (dq, *J* = 14.3, 7.1 Hz, 1H), 1.90 (d, *J* = 1.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.57, 137.56, 136.83, 136.61, 128.96, 128.60, 128.28, 128.15, 128.10, 126.61, 126.17, 66.76, 53.19, 37.68, 14.81.

HRMS (APCI) calcd forC20H21NNaO2 (M+Na⁺): 330.1465; found: 330.1468.



(E)-(2-methyl-3-propylhex-1-en-1-yl)benzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 7.6 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 6.26 (br, 1H), 2.14 (dt, J = 14.3, 4.8 Hz, 1H), 1.71 (d, J = 0.8 Hz, 3H), 1.49 – 1.23 (m, 9H), 0.90 (t, J = 7.1 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 141.38, 138.85, 129.08, 128.10, 126.20, 125.84, 49.40, 36.10, 20.94, 14.40, 13.32.

HRMS (APCI) calcd for C16H25 (M+H⁺):217.1951; found: 217.1950.

(S,E)-1-(2,3-dimethyl-4-phenylbut-3-en-1-yl)-3-(trifluoromethyl)benzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.33 (ddd, J = 19.6, 15.1, 7.6 Hz, 4H), 7.19 – 7.10 (m, 3H), 6.16 (s, 1H), 2.86 (dd, J = 13.4, 7.4 Hz, 1H), 2.70 (dd, J = 13.4, 7.3 Hz, 1H), 2.57 (dd, J = 14.1, 7.0 Hz, 1H), 1.82 (d, J = 0.8 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.45.

¹³C NMR (101 MHz, CDCl₃) δ 142.08, 141.58, 138.41, 132.63, 130.53 (q, *J* = 31.8 Hz), 128.97, 128.61, 128.12, 126.52 (q, *J* = 276.6 Hz), 126.10, 125.85 (q, *J* = 3.8 Hz), 125.54, 122.85 (q, *J* = 3.9 Hz), 45.41, 41.70, 19.14, 14.88.

HRMS (APCI) calcd for C19H20F3 (M+H+): 305.1512; found: 305.1511.



(E) - 1 - methoxy - 4 - ((4 - methyl - 5 - phenyl pent - 4 - en - 1 - yl) oxy) benzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 7.5 Hz, 2H), 7.25 – 7.16 (m, 3H), 6.89 – 6.73 (m, 4H), 6.32 (br, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.77 (d, J = 3.6 Hz, 3H), 2.43 – 2.32 (m, 2H), 2.09 – 1.94 (m, 2H), 1.90 (t, J = 4.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.76, 153.25, 138.45, 138.11, 128.83, 128.05, 125.94, 125.44, 115.51, 114.66, 68.06, 55.76, 36.97, 27.70, 17.80.

HRMS (APCI) calcd for C19H23O2 (M+H⁺):283.1693; found: 283.1692.



(E)-4-(1-(4-chlorophenyl)hept-1-en-2-yl)-1-tosylpiperidine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.30 – 7.20 (m, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.15 (s, 1H), 3.90 (d, J = 11.5 Hz, 2H), 2.45 (s, 3H), 2.26 (td, J = 11.9, 2.1 Hz, 2H), 2.11 (dd, J = 9.4, 6.7 Hz, 2H), 1.93 – 1.76 (m, 3H), 1.66 (ddd, J = 24.9, 12.4, 3.8 Hz, 2H), 1.34 (dd, J = 9.8, 5.6 Hz, 2H), 1.29 – 1.13 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.93, 143.40, 136.54, 133.00, 131.73, 129.78, 129.55, 128.17, 127.70, 123.11, 46.84, 42.04, 31.92, 31.02, 30.42, 28.44, 22.32, 21.48, 13.95.

HRMS (APCI) calcd for C25H32ClNNaO2S (M+Na⁺): 468.1735; found: 468.1734.



(R,E)-N-benzyl-2-ethyl-3-methyl-N,4-diphenylbut-3-enamide

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.15 (m, 11H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.00 – 6.90 (m, 2H), 5.86 (s, 1H), 4.90 (s, 2H), 2.94 (t, *J* = 7.2 Hz, 1H), 2.03 – 1.91 (m, 1H), 1.72 (s, 3H), 1.62 (dt, *J* = 13.6, 7.4 Hz, 1H), 0.87 (td, *J* = 7.3, 1.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.64, 142.32, 138.07, 137.96, 136.87, 129.33, 128.90, 128.44, 128.10, 128.01, 127.69, 127.37, 126.27, 54.75, 53.35, 24.78, 15.50, 12.52.

HRMS (APCI) calcd for C26H27NNaO (M+Na⁺): 392.1985; found: 392.1985.



(E)-3-(2-(1-tosylpiperidin-4-yl)hept-1-en-1-yl)pyridine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.25 (dd, J = 7.7, 4.9 Hz, 1H), 6.16 (s, 1H), 3.92 (d, J = 11.5 Hz, 2H), 2.45 (s, 3H), 2.27 (dd, J = 11.7, 10.2 Hz, 2H), 2.22 – 2.08 (m, 2H), 1.92 (d, J = 12.0 Hz, 1H), 1.84 (d, J = 12.8 Hz, 2H), 1.70 (td, J = 12.5, 3.6 Hz, 2H), 1.35 (dd,

J = 14.9, 7.3 Hz, 2H), 1.23 – 1.08 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.59, 148.98, 147.14, 143.52, 135.77, 133.88, 133.04, 129.64, 127.76, 123.11, 120.65, 46.87, 42.14, 31.95, 31.08, 30.60, 28.59, 22.41, 21.56, 14.00. HRMS (APCI) calcd for C24H32N2NaO2S (M+Na⁺): 435.2077; found: 435.2077.



(E)-4-(1-(naphthalen-2-yl)oct-1-en-2-yl)-1-tosylpiperidine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 11.8, 7.9 Hz, 3H), 7.68 (d, J = 8.2 Hz, 2H), 7.61 (s, 1H), 7.44 (ddd, J = 6.7, 5.5, 3.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.36 (s, 1H), 3.93 (d, J = 11.5 Hz, 2H), 2.45 (s, 3H), 2.27 (ddd, J = 20.1, 14.2, 5.1 Hz, 4H), 1.98 – 1.80 (m, 3H), 1.71 (dt, J = 30.5, 17.8 Hz, 2H), 1.41 (dd, J = 9.5, 5.4 Hz, 2H), 1.22 (td, J = 13.8, 5.5 Hz, 6H), 0.83 (t, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.73, 143.45, 135.70, 133.35, 133.10, 131.92, 129.61, 127.78, 127.53, 127.29, 126.94, 125.98, 125.49, 124.33, 46.97, 42.26, 31.57, 31.16, 30.65, 29.51, 28.94, 22.59, 21.55, 14.03.

HRMS (APCI) calcd for C30H37NNaO2S (M+Na⁺): 498.2437; found: 498.2437.



(E)-3-(oct-4-en-4-yl)-1-tosylpyrrolidine

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.03 (t, J = 7.0 Hz, 1H), 3.50 (dd, J = 9.6, 7.6 Hz, 1H), 3.40 (ddd, J = 9.9, 8.3, 2.8 Hz, 1H), 3.23 (td, J = 9.6, 6.7 Hz, 1H), 2.94 (t, J = 9.6 Hz, 1H), 2.69 – 2.51 (m, 1H), 2.44 (s, 3H), 2.01 – 1.78 (m, 5H), 1.72 – 1.45 (m, 1H), 1.38 – 1.13 (m, 4H), 0.93 – 0.67 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 143.40, 137.70, 134.34, 129.75, 127.60, 125.83, 52.48, 47.75, 44.70, 32.16, 30.75, 29.84, 23.06, 22.39, 21.64, 14.33, 13.94.

HRMS (APCI) calcd forC19H30NO2S (M+H⁺): 336.1992; found: 336.1992.



(E)-N-methyl-N-(2-methyl-3-propylhept-3-en-1-yl)aniline

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, J = 14.0, 6.7 Hz, 2H), 6.65 (t, J = 7.1 Hz, 3H), 5.18 (t, J = 7.1 Hz, 1H), 3.35 (dd, J = 14.6, 6.0 Hz, 1H), 3.14 (dd, J = 14.6, 8.5 Hz, 1H), 2.93 (s, 3H), 2.52 (dd, J = 14.2, 7.0 Hz, 1H), 2.23 – 1.91 (m, 4H), 1.36 (dt, J = 14.7, 7.4 Hz, 4H), 1.02 (d, J = 6.9 Hz, 2H), 0.98 – 0.84 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.47, 142.51, 129.19, 125.36, 115.59, 111.83, 59.32, 39.61, 38.85, 32.57, 30.02, 23.28, 22.81, 18.49, 14.59, 14.06.

HRMS (APCI) calcd for C18H30N (M+H⁺): 260.2373; found: 260.2375.

(E)-(4-(oct-4-en-4-yl)piperidin-1-yl)(phenyl)methanone

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.34 (m, 5H), 5.28 – 5.04 (m, 1H), 4.91 – 4.57 (m, 1H), 3.98 – 3.59 (m, 1H), 3.08 – 2.92 (m, 1H), 2.80 – 2.59 (m, 1H), 2.12 – 1.91 (m, 5H), 1.84 – 1.76 (m, 1H), 1.65 – 1.57 (m, 1H), 1.45 – 1.31 (m, 6H), 0.97 – 0.83 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 170.39, 142.53, 136.56, 129.54, 128.53, 127.01, 124.50, 48.58, 43.21, 43.08, 32.71, 32.14, 31.67, 29.92, 23.28, 22.66, 14.49, 13.98.

HRMS (APCI) calcd for C20H30NO (M+H⁺): 300.2322; found: 300.2323.



(3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyl-3a-((E)-2-methyl-3-phenylallyl)tetrahydro-5H-bis([1, 3]dioxolo)[4,5-b:4',5'-d]pyran

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.13 (m, 5H), 6.36 (br, 1H), 4.66 – 4.57 (m, 1H), 4.35 – 4.28 (m, 1H), 4.24 (d, *J* = 7.7 Hz, 1H), 3.99 – 3.88 (m, 1H), 3.75 (dd, *J* = 13.0, 3.2 Hz, 1H), 2.77 (dd, *J* = 13.5, 3.1 Hz, 1H), 2.62 (dd, *J* = 13.6, 3.1 Hz, 1H), 2.02 (d, *J* = 2.6 Hz, 3H), 1.68 – 1.44 (m, 6H), 1.39 – 1.31 (m, 6H).

 ^{13}C NMR (101 MHz, CDCl₃) δ 138.27, 134.06, 130.55, 129.05, 128.13, 126.26, 109.21, 108.12, 103.97, 72.31, 71.13, 70.76, 61.43, 49.89, 26.74, 26.13, 25.38, 24.30, 20.51.

HRMS(ESI) calcd for C21H28NaO5+ (M+Na⁺):383.1829; found: 383.1826.



1-((38,88,98,10R,138,148,178)-3-((Z)-1,2-diphenylvinyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,1 3,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one

Following general procedure, as a white solid. The assignment of 3β configuration in the major isomer was based on the large coupling constant. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.16 (m, 3H), 7.13 – 7.07 (m, 2H), 7.07 – 6.97 (m, 3H), 6.91 – 6.77 (m, 2H), 6.41 (br, 1H), 5.29 (d, *J* = 5.0 Hz, 1H), 2.53 (t, *J* = 8.9 Hz, 1H), 2.39 – 2.08 (m, 7H), 2.07 – 1.85 (m, 3H), 1.79 – 1.39 (m, 9H), 1.26 – 0.98 (m, 4H), 0.96 (s, 3H), 0.62 (s, 3H)

¹³C NMR (101 MHz, CDCl₃) δ 209.72, 147.97, 142.99, 141.27, 137.57, 129.15, 128.97, 128.54, 127.89, 126.88, 126.18, 124.88, 119.89, 63.85, 57.11, 50.42, 48.87, 44.14, 39.82, 39.00, 38.36, 37.17, 31.94, 31.93, 31.69, 28.12, 24.60, 22.92, 21.07, 19.70, 13.37.

HRMS calcd for C35H43O (M+H⁺): 479.3308; found: 479.3299.



(E)-4-(1-phenylprop-1-en-2-yl)-1-tosylpiperidine

Following general procedure, as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.3 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.22 – 7.16 (m, 3H), 6.24 (s, 1H), 3.98 – 3.61 (m, 2H), 2.44 (s, 3H), 2.27 (td, J = 11.8, 2.7 Hz, 2H), 1.99 – 1.87 (m, 1H), 1.84 – 1.65 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 143.58, 141.28, 138.17, 133.23, 129.73, 129.00, 128.17, 127.89, 126.26, 124.60, 46.82, 45.45, 30.25, 21.67, 16.02.

HRMS (APCI) calcd for C21H25NNaO2S (M+Na⁺): 378.1498; found: 378.1499.



((1E,7Z)-2-methyldeca-1,7-dien-1-yl)benzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, J = 14.6, 7.1 Hz, 2H), 7.23 (d, J = 7.1 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.26 (s, 1H), 5.45 – 5.16 (m, 2H), 2.16 (dd, J = 15.4, 7.8 Hz, 2H), 2.10 – 1.94 (m, 4H), 1.85 (s, 3H), 1.57 – 1.46 (m, 2H), 1.44 – 1.33 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 139.37, 138.81, 131.88, 129.23, 128.94, 128.12, 125.88, 124.91, 40.74, 29.51, 27.70, 27.11, 20.68, 17.85, 14.55.

HRMS (APCI) calcd for C17H24Na+ (M+Na⁺): 251.1770; found: 251.1773.

Ph

(S,E)-(3-cyclopentyl-2-methylpent-1-en-1-yl)benzene

Following general procedure, as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 6.2 Hz, 2H), 7.16 (dt, *J* = 9.6, 7.7 Hz, 1H), 6.25 (s, 1H), 1.84 (m, 2H), 1.76 – 1.66 (m, 3H), 1.65 – 1.42 (m, 6H), 1.39 – 1.23 (m, 2H), 1.21 – 1.10 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.93, 138.80, 128.98, 127.96, 126.60, 125.68, 58.39, 43.51, 31.55, 31.53, 25.36, 25.03, 24.63, 13.53, 12.34, 0.00.

HRMS (APCI) calcd for C17H24Na+ (M+Na⁺): 251.1770; found: 251.1772.

c) X-Ray Structure



Supplementary Table 1 Crystal data and structure refinement.

Empirical formula	C21H25NO2S
Formula weight	355.48
Temperature	291(2)

Wavelength	1.54184
Crystal system,	Triclinic
space group	2 P -1 -P 1
Unit cell dimensions	$a = 11.5338(4)$ Å $\alpha = 87.998(2)$
b = 14.1735(3) Å β = 84.767(2)	
$c = 22.2327(5) \text{ Å } \gamma = 81.745(2)$	
Volume	3580.95(17) Å3
Z, Calculated density	2, 1.128 Mg/m3
Absorption coefficient	0.617
F(000)	1322
Crystal size	$0.26 \times 0.22 \times 0.21 \text{ mm3}$
Theta range for data collection	3.694 to 71.4610
Limiting indices	-13<=h<=14, -17<=k<=15, -25<=l<=27
Reflections collected / unique	13299/11177 [R(int) = 0.0293]
Completeness to theta $= 67.684$	98.6%
Absorption correction	multi-scan
Max. and min. transmission	0.86136 and 1.00000
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	13299/55/827
Goodness-of-fit on F2	1.060
Final R indices [I>2sigma(I)]	R = 0.0757, wR = 0.2051
R indices (all data)	R = 0.0857, wR = 0.2148
Radiation type	Cu/Ka
Largest diff. peak and hole	0.613 and -0.822 e.Å

Supplementary Table 2 Selective data of atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å² × 10^3).

X	Y	Ζ	U(eq)	
-3337.9(3)	1824.5(6)	-532.5(4)	677(2)	
-2491.4(8)	1886.2(17)	1116(12)	569(4)	
-3682.0(10)	3279.4(18)	-254.5(17)	975(6)	
-3303.1(9)	1473(2)	-16380(12)	896(5)	
0984.4(9)	2739(2)	1471.4(13)	511(4)	
-3753.9(9)	193(2)	21.0(15)	557(4)	
-2391.5(11)	2328(2)	1263.7(16)	623(5)	
	x -3337.9(3) -2491.4(8) -3682.0(10) -3303.1(9) 0984.4(9) -3753.9(9) -2391.5(11)	xY-3337.9(3)1824.5(6)-2491.4(8)1886.2(17)-3682.0(10)3279.4(18)-3303.1(9)1473(2)0984.4(9)2739(2)-3753.9(9)193(2)-2391.5(11)2328(2)	xYz $-3337.9(3)$ $1824.5(6)$ $-532.5(4)$ $-2491.4(8)$ $1886.2(17)$ $1116(12)$ $-3682.0(10)$ $3279.4(18)$ $-254.5(17)$ $-3303.1(9)$ $1473(2)$ $-16380(12)$ $0984.4(9)$ $2739(2)$ $1471.4(13)$ $-3753.9(9)$ $193(2)$ $21.0(15)$ $-2391.5(11)$ $2328(2)$ $1263.7(16)$	xYzU(eq) $-3337.9(3)$ $1824.5(6)$ $-532.5(4)$ $677(2)$ $-2491.4(8)$ $1886.2(17)$ $1116(12)$ $569(4)$ $-3682.0(10)$ $3279.4(18)$ $-254.5(17)$ $975(6)$ $-3303.1(9)$ $1473(2)$ $-16380(12)$ $896(5)$ $0984.4(9)$ $2739(2)$ $1471.4(13)$ $511(4)$ $-3753.9(9)$ $193(2)$ $21.0(15)$ $557(4)$ $-2391.5(11)$ $2328(2)$ $1263.7(16)$ $623(5)$

C3	-1059.4(9)	1507(2)	1440.2(13)	505(4)
C6	-274.2(10)	1987(2)	1853.9(12)	521(4)
C5	-2015.5(10)	540(2)	-90.6(15)	611(5)
C4	-1223.1(10)	1043(2)	248.2(14)	593(5)
C20	-3681.9(10)	-1341(2)	-384.3(16)	617(5)
C2	-1603.7(11)	2825(2)	164.07(15)	599(4)
C12	2006.2(12)	4286(3)	1046.7(19)	770(6)
C18	-4290.3(10)	-2481(3)	993.1(18)	672(5)
C7	207.4(9)	2293(2)	1202.3(13)	516(4)
C9	1464.1(12)	2065(2)	2334.0(16)	660(5)
C13	1279.1(10)	3840(3)	830.4(15)	637(5)
C16	-4099.5(11)	401(3)	915.8(18)	712(5)
C19	-3948.9(11)	-2647(2)	981(17)	667(5)
C11	2463.2(11)	3619(3)	1903(2)	771(6)
C17	-4363.2(11)	-944(3)	1382.0(18)	762(6)
C10	2197.0(12)	2511(3)	2535.0(19)	787(6)
C14	-90.6(13)	2105(4)	3069.4(15)	868(8)
C21	-4572.9(14)	-3926(3)	1526(2)	991(9)

Table 3 Anisotropic Displacement Parameters $(\text{\AA}^2 \times 10^3)$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2a^{*2}U^{11}+...+2\text{hka}\times b\times U12]$.

Atom	U11	U22	U33	U23	U13	U12
S 1	69.7(3)	54.5(3)	74.8(3)	10.7(2)	-0. 8(2)	-4.7(2)
N1	61.7(9)	49.8(8)	59.5(8)	-2.6(6)	10.5(7)	-7.0(6)
O2	91.0(12)	52.5(8)	140.2(16)	10.1(9)	-6.5(10)	12.2(8)
01	99.3(12)	101.7(12)	61.6(8)	18.3(8)	-5.3(8)	-24.6(10)
C8	59.5(10)	48.2(9)	44.9(8)	-5.6(7)	6.7(7)	0.1(7)
C15	47.9(9)	53.5(9)	64.7(10)	-0.0016(8)	5.7(7)	0.2(7)
C1	67.9(11)	58.6(10)	62.7(10)	-10.0(8)	17.1(9)	-0.6(9)
C3	63.8(10)	46.1(8)	43.9(8)	-2.0(6)	15.5(7)	7.7(7)
C6	66.2(10)	50.0(9)	40.4(8)	-2.9(6)	9.6(7)	-7.5(7)
C5	64.9(11)	61.1(10)	58.6(10)	-18.1(8)	13.6(8)	-10.2(9)
C4	60.3(10)	66.4(11)	53.0(9)	-18.1(8)	15.0(8)	-10.0(9)
C20	60.2(10)	59.2(10)	66.7(11)	-7.4(9)	13.2(8)	-4.2(9)

C2	73.5(12)	54.5(9)	52.7(9)	-13.4(8)	13.8(8)	-5.0(9)
C12	65.1(12)	84.2(15)	82.7(14)	-0. 3(11)	14.7(10)	-15.9(11)
C18	48.7(10)	72.9(12)	76.2(12)	1.31(10)	-1.3(8)	-7.9(9)
C7	60.9(10)	52.9(9)	40.8(8)	-2.8(7)	7.2(7)	-3.9(8)
C9	76.2(13)	55.7(10)	63.2(11)	3.7(8)	3.3(9)	7.7(9)
C13	59.3(10)	74.3(12)	57.1(10)	8.2(9)	8.2(8)	-6.1(9)
C16	62.5(11)	66.7(12)	85.9(14)	-11.0(10)	16.6(10)	6.0(10)
C19	63.2(11)	54.2(10)	80.3(13)	-2.6(9)	4.5(9)	-5.2(9)
C11	55.4(11)	81.1(14)	91.6(15)	-24.0(12)	2.8(10)	-0.6(10)
C17	59.2(11)	99.0(17)	73.6(13)	1.3(12)	20.4(10)	0.3(11)
C10	72.1(13)	82.2(15)	73.7(13)	-11.4(11)	-12.2(10)	21.3(12)
C14	80.7(14)	139(2)	41.3(10)	-4.9(11)	11.6(9)	-24.0(15)
C21	82.6(16)	105.2(19)	104.1(18)	38.4(16)	-0.4(13)	-24.1(15)

Table 4 Bond Lengths.

S1 O1	1.4249(17)	C5 C4	1.517(2)
S1 O2	1.4335(17)	C5 H5A	0.9700
S1 N1	1.6407(16)	C5 H5B	0.9700
S1 C15	1.7544(18)	C4 H4A	0.9700
N1 C1	1.468(2)	C4 H4B	0.9700
N1 C5	1.469(2)	C20 C19	1.371(3)
C8 C13	1.385(3)	C20 H2	0 0.9300
C8 C9	1.396(3)	C2 H2A	0.9700
C8 C7	1.470(2)	C2 H2B	0.9700
C15 C20	1.384(3)	C12 C11	1.367(3)
C15 C16	1.389(3)	C12 C13	1.379(3)
C1 C2	1.514(3)	C12 H12	0.9300
C1 H1A	0.9700	C18 C17	1.378(3)
C1 H1B	0.9700	C18 C19	1.380(3)
C3 C6	1.514(2)	C18 C21	1.506(3)
C3 C4	1.521(2)	C7 H7	0.9300
C3 C2	1.535(2)	C9 C10	1.389(3)
C3 H3	0.9800	С9 Н9	0.9300
C6 C7	1.328(2)	C13 H13	0.9300

C6 C14	1.505(2)	C16 C17	1.385(3)
C14 H14A	0.9600	C16 H16	0.9300
C14 H14B	0.9600	C19 H19	0.9300
C14 H14C	0.9600	C11 C10	1.357(3)
C21 H21A	0.9600	C11 H11	0.9300
C21 H21B	0.9600	C17 H17	0.9300

Table 5 Bond Angle.

01	S 1	O2	120.04(11)	C1	C2	H2B	109.1
01	S 1	N1	106.87(9)	C3	C2	H2B	109.1
O2	S 1	N1	106.35(9)	H2A	C2	H2B	107.9
01	S 1	C15	108.56(9)	C11	C12	C13	120.2(2)
O2	S 1	C15	108.14(11)	C11	C12	H12	119.9
N1	S 1	C15	106.04(8)	C13	C12	H12	119.9
C1	N1	C5	112.09(15)	C17	C18	C19	117.6(2)
C1	N1	S 1	116.43(12)	C17	C18	C21	121.2(2)
C5	N1	S 1	116.32(11)	C19	C18	C21	121.3(2)
C13	C8	C9	116.74(18)	C6	C7	C8	129.69(15)
C13	C8	C7	119.84(16)	C6	C7	H7	115.2
C9	C8	C7	123.37(17)	C8	C7	H7	115.2
C20	C15	C16	119.64(18)	C10	C9	C8	120.7(2)
C20	C15	S 1	119.28(15)	C10	C9	H9	119.6
C16	C15	S 1	120.86(15)	C8	C9	H9	119.6
N1	C1	C2	109.41(14)	C12	C13	C8	121.89(19)
N1	C1	H1A	109.8	C12	C13	H13	119.1
C2	C1	H1A	109.8	C8	C13	H13	119.1
N1	C1	H1B	109.8	C17	C16	C15	118.7(2)
C2	C1	H1B	109.8	C17	C16	H16	120.6
H1A	C1	H1B	108.2	C15	C16	H16	120.6
C6	C3	C4	115.25(13)	C20	C19	C18	121.7(2)
C6	C3	C2	112.11(14)	C20	C19	H19	119.2
C4	C3	C2	108.06(15)	C18	C19	H19	119.2
C6	C3	H3	107	C10	C11	C12	119.5(2)
C4	C3	H3	107	C10	C11	H11	120.2
C2	C3	H3	107	C12	C11	H11	120.2
C7	C6	C14	123.01(17)	C18	C17	C16	122.3(2)
C7	C6	C3	123.01(14)	C18	C17	H17	118.8
C14	C6	C3	113.98(15)	C16	C17	H17	118.8
N1	C5	C4	108.86(14)	C11	C10	C9	120.9(2)
N1	C5	H5A	109.9	C11	C10	H10	119.6
C4	C5	H5A	109.9	C9	C10	H10	119.6

N1	C5	H5B	109.9	C6	C14	H14A	109.5
C4	C5	H5B	109.9	C6	C14	H14B	109.5
H5A	C5	H5B	108.3	H14A	C14	H14B	109.5
C5	C4	C3	111.75(14)	C6	C14	H14C	109.5
C5	C4	H4A	109.3	H14A	C14	H14C	109.5
C3	C4	H4A	109.3	H14B	C14	H14C	109.5
C5	C4	H4B	109.3	C18	C21	H21A	109.5
C3	C4	H4B	109.3	C18	C21	H21B	109.5
H4A	C4	H4B	107.9	H21A	C21	H21B	109.5
C19	C20	C15	120.08(18)	C18	C21	H21C	109.5
C19	C20	H20	120	H21A	C21	H21C	109.5
C15	C20	H20	120	H21B	C21	H21C	109.5
C1	C2	C3	112.35(14)	C3	C2	H2A	109.1

Table 6 Torsion Angles.

01	S 1	N1	C1	176.55(14)
O2	S 1	N1	C1	47.19(16)
C15	S 1	N1	C1	-67.77(15)
01	S 1	N1	C5	-47.85(15)
O2	S 1	N1	C5	-177.21(14)
C15	S 1	N1	C5	67.82(14)
01	S 1	C15	C20	29.22(18)
O2	S 1	C15	C20	160.96(15)
N1	S 1	C15	C20	-85.31(16)
01	S 1	C15	C16	-156.26(16)
O2	S 1	C15	C16	-24.52(19)
N1	S 1	C15	C16	89.22(17)
C5	N1	C1	C2	59.8(2)
S 1	N1	C1	C2	-162.76(13)
C4	C3	C6	C7	12.6(2)
C2	C3	C6	C7	-111.52(19)
C4	C3	C6	C14	-167.99(18)
C2	C3	C6	C14	67.9(2)
C1	N1	C5	C4	-61.10(19)
S 1	N1	C5	C4	161.45(12)
N1	C5	C4	C3	59.0(2)
C6	C3	C4	C5	178.60(15)

C2	C3	C4	C5	-55.1(2)
C16	C15	C20	C19	-0.2(3)
S 1	C15	C20	C19	174.40(14)
N1	C1	C2	C3	-56.3(2)
C6	C3	C2	C 1	-178.02(14)
C4	C3	C2	C 1	53.91(19)
C14	C6	C7	C8	1.9(3)
C3	C6	C7	C8	-178.75(17)
C13	C8	C7	C6	-142.8(2)
C9	C8	C7	C6	39.5(3)
C13	C8	C9	C10	0.9(3)
C7	C8	C9	C10	178.66(17)
C11	C12	C13	C8	1.2(3)
C9	C8	C13	C12	-1.7(3)
C7	C8	C13	C12	-179.52(18)
C20	C15	C16	C17	0.1(3)
S 1	C15	C16	C17	-174.38(15)
C15	C20	C19	C18	-0.3(3)
C17	C18	C19	C20	0.8(3)
C21	C18	C19	C20	-179.19(19)
C13	C12	C11	C10	0.2(3)
C19	C18	C17	C16	-0.9(3)
C21	C18	C17	C16	179.1(2)
C15	C16	C17	C18	0.4(3)
C12	C11	C10	C9	-1.0(3)
C8	C9	C10	C11	0.4(3)



IV. NMR Spectra































42.09 42.03 44.58 43.01 42.89 42.89 42.89 42.89 42.89 42.83 42.85 42.83 42.85 42.83 42.85 42.83 42.85 42.83

